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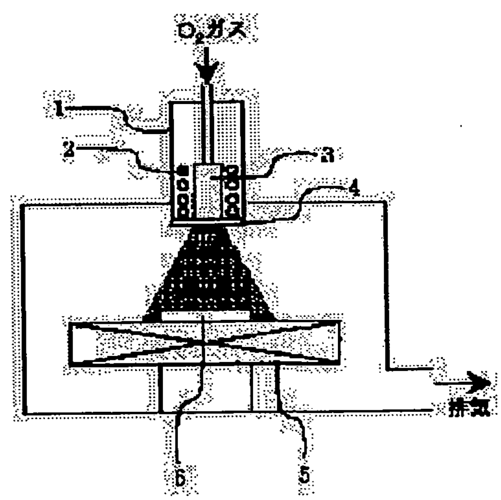
(54) HEAT TREATMENT METHOD OF OXIDE THIN FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To repair oxygen deficiency without causing ion damage, by a method wherein, when a tantalum oxide film is heat-treated in an oxidizing atmosphere, the heat treatment is performed by irradiating the tantalum oxide film with atomic state oxygen.

SOLUTION: A radical source 1 which can produce electrically neutral oxygen radicals by RF electrodeless discharge is introduced. By applying high frequency power of 13.56MHz to an RF coil 2, discharge is caused in oxygen in a discharge tube 3. Gas molecules which have generated plasma discharge dissociate as a result of collision against the inner wall of the discharge tube 3, and turn to active atomic state oxygen (oxygen radicals). A specimen 6 is irradiated with the oxygen radicals which are released in a vacuum chamber from small holes of an aperture plate 4. Ion concentration in oxygen radicals decreases. Heat treatment temperature at 300° C or higher is effective. Oxygen deficiency repairing effect increases as the temperature becomes higher. Heat treatment is performed at 600° C or lower for at most 10 minutes. Oxygen deficiency can be repaired without causing ion damage in a Ta2O5 film.



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CLAIMS

[Claim(s)]
[Claim 1] It is the heat treatment approach of the oxide thin film characterized by being the approach of heat-treating the tantalic acid-ized film in an oxidizing atmosphere, and performing heat treatment by irradiating atom-like oxygen at said tantalic acid-ized film.
[Claim 2] It is the heat treatment approach of the oxide thin film characterized by being the approach of heat-treating the tantalic acid-ized film in an oxidizing atmosphere, and performing heat treatment by irradiating the atom-like oxygen generated by RF electrodeless discharge at said tantalic acid-ized film.
[Claim 3] The heat treatment approach of an oxide thin film that the concentration of the ion-like oxygen contained in the ambient atmosphere of said heat treatment in claim 1 is 10% or less to said atom-like oxygen.
[Claim 4] The heat treatment approach of an oxide thin film that the thing with the luminescence wavelength of 750nm or more is contained 90% or more in claim 1 in the atom-like oxygen contained in the ambient atmosphere of said heat treatment.
[Claim 5] It is the heat treatment approach of an oxide thin film that said heat treatment is performed in claim 1 at 300-degree-C or more temperature of 700 degrees C or less.

[Translation done.]

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2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the heat treatment approach of an oxide thin film.

[0002]

[Description of the Prior Art] Using Ta 2O5 (tantalum pentoxide) which is a high dielectric constant insulator layer as a capacity insulator layer of a semiconductor memory is examined. In that case, since it aims at forming on the electrode of three-dimensional structure, the chemical vapor deposition which used the organic compound (for example, pentaethoxy tantalum) of a tantalum as the raw material is used. However, when 2OTa5 film is formed, there is much impurity carbon mixed from an oxygen deficiency or a raw material, and since leakage current is very large, heat treatment after formation is indispensable.

[0003] For restoration of an oxygen deficiency, or removal of impurity carbon, the inside of an oxygen ambient atmosphere 700 degrees C or more usually needs to be heat-treated. However, above 700 degrees C, 2OTa5 film will crystallize and increase of the leakage current by the grain boundary will arise. Then, in order to restore an oxygen deficiency effectively also at low temperature (700 degrees C or less), the heat treatment approach in an active oxygen ambient atmosphere was considered. For example, the approach of exciting an oxygen molecule in ozone beforehand, conveying to a heat treatment room, exciting it with a low-pressure mercury lamp in the processing interior of a room, making generate an oxygen radical, and heat-treating by the plasma, was devised (the UV ozone heat-treating method).

[0004] as these well-known examples — JP,2-283022,A — "— a technical digest — OBU symposium ON BUIERU S eye technology (TechnicalDigest of Symposium on VLSI Technology) and p.25(1989)" are mentioned. moreover — as the approach (oxygen plasma heat approach) of heat-treating, while activating oxygen with the plasma and putting 2OTa5 film into the plasma — JP,4-199828,A — "— EKUSU ten dead abs truck shoes — OBU conference ON solid-state debye SUIZU and MATERIARUZU (Extended Abstracts of Conference on Solid State Devides and Materials), and p.862(1993)" are mentioned.

[0005]

[Problem(s) to be Solved by the Invention] The typical example of equipment of the UV ozone heat-treating method is shown in drawing 2 . It is the approach of exciting an oxygen molecule in ozone beforehand, conveying to a heat treatment room, exciting it with a low-pressure mercury lamp 8 in the processing interior of a room, making generate an oxygen radical, and heat-treating with a plasma generator 7. In order to fully restore an oxygen deficiency, it is necessary to elevated-temperature-ize heat treatment temperature but, and if ozone elevated-temperature-izes substrate temperature at the time of heat treatment at 300 degrees C or more by this approach in order to dissociate it in an oxygen molecule easily above 300 degrees C, the oxygen deficiency restoration effectiveness will become small. Therefore, the approach whose heat treatment in an elevated temperature is attained is required.

[0006] Next, the typical example of equipment of an oxygen plasma heat approach is shown in drawing 3 . It is the approach of heat-treating, while activating oxygen with a plasma generator 7 and putting 2OTa5

film into the plasma. Since it can continue generating an oxygen radical on a substrate front face whenever it is this approach, even if it elevated-temperature-izes substrate temperature at 300 degrees C or more, there is the oxygen deficiency restoration effectiveness. However, since oxygen ion is also generated by the plasma, 2OTa5 film will receive ion damage, and the factor of new leakage current will arise. Therefore, the oxygen deficiency was restored without doing damage to 2OTa5 film, and the heat treatment approach that leakage current could be reduced effectively was searched for.

[0007] After performing oxygen plasma heat treatment and forming a capacitor by our examination furthermore, when it let it pass like the 450-degree C heat process, it turned out that the leakage current of a capacitor increases. It is for producing the defect which the impurity carbon mixed from a raw material into Ta2O5 film is mixing several % to about dozens of% as mentioned above, association is cut as easily as the heat process which is about 450 degrees C, and causes leakage current. When adopting 2OTa5 film as a capacity insulator layer of a semi-conductor storage element, and a wiring process is taken into consideration, the thermal resistance of 450 degrees C or more is needed. Then, the strong carbon to carbon bond which is not cut at least about 450 degrees C could be formed, and the heat treatment approach of not increasing leakage current even like the heat process after capacitor formation was searched for.

[0008]

[Means for Solving the Problem] In order to solve the two above-mentioned technical problems, the oxygen radical heat-treating method was devised. This is the approach of irradiating 2OTa5 film in which was made to generate neutrality atom-like oxygen (oxygen radical) electrically, and the temperature up was carried out by RF electrodeless discharge. An oxygen deficiency can be restored by using this heat treatment approach, without making 2OTa5 film generate ion damage. Moreover, since the oxidizing power to carbon is strong, even the temperature of 700 degrees C or less can carry out oxidation removal of the carbon in Ta2O5 film, and the carbon which remained into the film will also be in the integrated state which is not cut easily. Therefore, even if it lets it pass like the about 450-degree C heat process after capacitor formation, 2OTa5 film with little increase of leakage current can be formed.

[0009]

[Function] An oxygen deficiency can be restored without producing ion damage, and, in addition, even low temperature 700 degrees C or less can fully realize removal or strong association for the impurity carbon in the film.

[0010]

[Example] The thermal treatment equipment for carrying out this invention is shown in drawing 1 . It has the sample base 5 equipped with the substrate heating heater, and Rhine which introduces oxygen gas. The flow rate of oxygen is controlled by the massflow controller. As an exhaust air system, it has the turbo Morecular pump and the rotary pump, and can exhaust to 10-8Torr. Moreover, it has the source 1 of a radical which can generate a neutrality oxygen radical electrically by RF electrodeless discharge. Oxygen is introduced in the discharge tube 3 and it is 13.56MHz to RF coil 2. The oxygen in the discharge tube is made to cause discharge by impressing high-frequency power. The gas molecule which caused plasma discharge is dissociated by the collision with the wall of the discharge tube, serves as activity atom-like oxygen (oxygen radical), is emitted in a vacuum chamber from the small hole (0.5mm) of the aperture plate 4 made from an alumina, and is irradiated by the sample 6.

[0011] In order to identify the active species generated from the source of an oxygen radical, plasma spectral analysis was performed. The spectroscope used high sensitivity multi-channel spectrometry equipment. Arrangement was changed so that the source of a radical beam might come to the transverse plane of an inspection hole in the case of spectral analysis, the detector was set over the inspection hole, and even the spectroscope measured using arrangement of drawing light, with the optical fiber.

[0012] A measurement result is shown in drawing 4 . The wavelength of 394.7nm, 436.9nm, 532.9nm, 615.8nm, 645.7nm, 700.2nm, 725.5nm, and 777.5nm are luminescence by the oxygen radical. The wavelength of 525.1nm which is luminescence according to oxygen ion as compared with it, 559.7nm, and

597.3nm Concentration [as opposed to / a peak is very small and / an oxygen radical at least] is 0.1%. It was the following. 777.5nm luminescence which is the largest peak here is the oxygen radical which supported luminescence by the transition to 3s5S0 (principal quantum number = 3 or 5-fold term S) from 3p5P (principal quantum number = 3 or 5-fold term P), and was excited about 11eV from the ground state. An oxygen radical with this luminescence demonstrates big effectiveness to impurity carbon removal and oxygen deficiency restoration of 2OTa5 film. It was 90% or more which has luminescence of 750nm or more in atom-like oxygen.

[0013] The production procedure of the sample used in order to prove the effectiveness of the heat treatment approach by this invention is explained. Sample structure is shown in drawing 5 . The Si substrate 9 is 0.01-ohmcm with n mold. The thing of low resistance of extent was used. First, it was made to rinse and dry after checking dipping for 2 minutes and carrying out a water break into HF solution diluted to 1/20. Then, as a lower electrode 10, using SiH4, H2, and PH3 as material gas, 200nm of Si film which doped 4x1020 P per three (Lynn)·1cm is formed with a CVD method, and it is N2. 800 degrees C and polycrystal-ization for 10 minutes were performed in the ambient atmosphere. Furthermore, it is NH4. 800 degrees C and the nitriding for 1 minute were performed in the ambient atmosphere, and about 2nm of a polycrystal-ized Si front face was changed into the Si nitride 11. This is for controlling that a lower electrode oxidizes and capacity falls by heat treatment under Ta2O5 film formation and after formation. Then, 2OTa5 film 12 was formed by chemical vapor deposition. A pentaethoxy tantalum (heating and carrier gas are N2:50sccm to 125 degrees C about a raw material container) and oxygen (600sccm) were used as the raw material, and it formed 8nm of thickness at membrane formation room pressure force 0.2Torr and the substrate temperature of 420 degrees C.

[0014] Then, the conventional example was heat-treated with heat treatment by this invention for the comparison, and the up electrode was formed for evaluation of electrical characteristics. The up electrode formed 50nm of TiN film 13 with the CVD method which uses TiCl4 and NH4 as a raw material, and processed it into 100-micrometer angle by the well-known lithography / etching method.

[0015] The voltage-current consistency property of 2OTa5 film which heat-treated by this invention is shown in drawing 6 as compared with other heat treatment approaches. UV ozone heat treatment conditions were made into the substrate temperature of 280 degrees C, and the pressure was made into ordinary pressure. Oxygen plasma-heat-treatment conditions are the substrate temperature of 400 degrees C, pressure 10Torr, and RF frequency of 13.56MHz. It carried out. The conditions of oxygen radical heat treatment are the substrate temperature of 400 degrees C, pressure 10-6Torr, and RF frequency of 13.56MHz. It carried out. In any case, heat treatment time amount unified in 10 minutes. Each SiO2 conversion thickness was 2.5nm.

[0016] As drawing 6 shows, the oxygen radical heat-treating method by this invention is understood that the reduction effectiveness of the leak current density of 2OTa5 film is large compared with other heat-treating methods. The thing with the larger leakage current reduction effectiveness than the UV ozone heat-treating method is because-izing of the heat treatment temperature can be carried out [elevated temperature]. Moreover, the thing with the larger leakage current reduction effectiveness than an oxygen plasma heat approach is for not receiving damage by oxygen ion.

[0017] The more there is little concentration of the oxygen ion to an oxygen radical, the effect of ion damage is small and, the more it has the effectiveness of leakage current reduction. 1.25V needed for DRAM actuation as shown in drawing 7 In order to have pressure-proofing, it is necessary to make an ion-like oxygen density 10% or less. It is 0.1V if an ion-like oxygen density is stopped to 1% or less. If it can have proof-pressure allowances and stops to 0.1% or less still more desirably, it can have the proof-pressure allowances of 0.2V.

[0018] Next, it let it pass like the heat process for 450 degrees C and 90 minutes in nitrogen-gas-atmosphere mind after capacitor formation, and the voltage-current consistency property was evaluated again. A result is shown in drawing 8 . What performed oxygen radical heat treatment to leakage current increasing greatly like a 450-degree C heat process, as for what performed oxygen plasma heat treatment has small increase of leakage current. Since the oxidizing power of an oxygen radical to

carbon is strong, it is because the carbon which the oxidation removal of the carbon in Ta2O5 film could be carried out, and remained into the film would also be in the integrated state which is not cut easily. Therefore, 2OTa5 film with little increase of leakage current has been formed also by 450-degree C heat treatment after capacitor formation.

[0019] The temperature-programmed-desorption analysis result of the carbon in Ta2O5 film which performed the oxygen plasma and oxygen radical heat treatment, respectively is shown in drawing 9 . The measurement result of 2OTa(as-depo) 5 film which has not heat-treated for a comparison is also shown. In as-depo, it is CH4 [the desorption of CH4 and CO is observed in / large / 100 to 700 degrees C, and / CO]. There is much desorption. It ****s between 100 degrees C and 400 degrees C, and it is CH4 which performed oxygen plasma heat treatment. It compares and the desorption of CO increases. This is for the carbon in Ta2O5 film carrying out weak oxygen association by the oxygen plasma, and becoming easy to **** easily. This carbon from which it is desorbed is the cause of increasing leakage current like the heat process after capacitor formation. There is little desorption of CO compared with oxygen plasma heat treatment, and it is CH4 which performed oxygen radical heat treatment. Desorption is not observed. As mentioned above, since the oxidizing power of an oxygen radical to carbon is strong, this is because the oxidation removal of the carbon in Ta2O5 film was fully carried out. Moreover, since the carbon which remains in the film will also be in the strong integrated state which is not cut easily, below 700 degrees C, it is thought that it was hard that it comes to ****.

[0020] Here, it adds about the sequence of the oxygen radical heat-treating method. There are an approach of suspending an oxygen radical exposure, after lowering the temperature to about 200 degrees C, and the approach of starting a temperature fall, after suspending an oxygen radical exposure after heat treatment termination of predetermined time. In order that the impurity carbon which remains in Ta2O5 film may oxidize further in the case of the former, like the heat process after capacitor formation, there is carbonaceous desorption and leak current density increases a little. In the example, this procedure is performing oxygen radical heat treatment. Since it will be shut up without the carbon in Ta2O5 film oxidizing if the latter approach is used, degradation depended like a heat process is lost. However, since it will be left in a vacuum (or inside of an oxygen molecule) at an elevated temperature and the desorption of the oxygen in Ta2O5 film etc. arises, an initial property is inferior compared with what is depended on the former approach. It is a design matter which approach is used as a result by there being no great difference in next electrical characteristics as the heat process after capacitor formation.

[0021] Oxygen radical heat treatment temperature is effective above 300 degrees C, and 2OTa5 film with little degradation which the oxygen deficiency restoration effectiveness and the impurity carbon removal effectiveness depend like low leak and a heat process by becoming large is obtained, so that it elevated-temperature-izes. However, above 700 degrees C, since 2OTa5 film crystallizes and the leakage current increase from the grain boundary arises, heat treatment temperature is limited to 700 degrees C or less. Moreover, since growth of the silicon oxide in the silicon of a substrate and the interface of Ta 2O5 will become remarkable and capacity will fall if it becomes an elevated temperature, 600 degrees C or less of heat treatment temperature are desirable. Moreover, the allowable temperature of the heat process after capacitor formation is 700 degrees C or less, and if it is possible, 550 degrees C or less are desirable [allowable temperature].

[0022] About oxygen radical heat treatment time amount, the oxygen deficiency restoration effectiveness and the impurity carbon removal effectiveness become large, so that it carries out for a long time, and 2OTa5 film with little degradation depended like low leak and a heat process is obtained. However, heat treatment temperature is limited in 30 or less minutes, and if it is possible, 10 or less minutes is desirable [heat treatment temperature], since growth of the silicon oxide in the silicon of a substrate and the interface of Ta 2O5 will become remarkable and capacity will fall, if it becomes in 30 minutes or more.

[0023] Although the chemical vapor deposition which used the pentaethoxy tantalum as the raw material as a method of depositing 2OTa5 film was used in the example, effectiveness was checked also for

2OTa5 film which formed the raw material of Ta using other Ta organic substance sources, such as Ta (OCH3)5 and Ta (N(CH3) 2)5.

[0024] Although polycrystalline silicon was used as a lower electrode of a capacitor here, the same effectiveness was acquired even if it used the metallic material, for example, W and Pt, instead of it.

[0025] Pt and W can be used also about an up electrode in addition to TiN. It is not what was restricted to CVD also about the formation approach, and a spatter may be used.

[0026] Furthermore, dynamic random access memory (DRAM) was produced using the oxygen radical heat-treating method by this invention. The sectional view of a memory cell is shown in drawing 10 . Here, it is a capacitative element SiO2. It was satisfied with 2.5nm (8nm of 2OTa5 thickness) of conversion thickness of proof-pressure 1.25V (judgment current density 10-8 A/cm2), and the actuation as a DRAM was checked further. As lower electrode structure, although the thick-film mold was used here, even if it uses cylindrical and a fin mold, the same effectiveness is acquired.

[0027] The capacitative element formed of this invention is applicable also to the capacitor part which needs large capacity by LSI for a communication link etc.

[0028] Furthermore, only as a capacitative element, even if it applies to the formation process of the gate oxide of MOS, the oxide film which has withstand voltage higher than the conventional approach is obtained.

[0029]

[Effect of the Invention] According to this invention, even if leakage current was small and let it pass like the heat process which is 450 degrees C after capacitor formation compared with the UV ozone heat-treating method or the oxygen plasma heat approach, it enabled increase of leakage current to produce little 2OTa5 film.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The explanatory view of the example of an oxygen radical thermal treatment equipment.
[Drawing 2] The explanatory view of the UV ozone heat-treating method of the thermal treatment equipment by the conventional technique.
[Drawing 3] The explanatory view of the oxygen plasma heat approach of the thermal treatment equipment by the conventional technique.
[Drawing 4] The emission spectrum property Fig. of an oxygen radical.
[Drawing 5] The explanatory view of sample structure used for electrical-characteristics evaluation.
[Drawing 6] The property Fig. showing the voltage-current consistency property after radical heat treatment as compared with the conventional approach.
[Drawing 7] The property Fig. of a pressure-proof ion-like oxygen density dependency.
[Drawing 8] A heat process is the voltage-current consistency property Fig. of order.
[Drawing 9] The property Fig. of a temperature-programmed-desorption analysis result.
[Drawing 10] The sectional view of the important section of DRAM which carried out **** production for oxygen radical heat treatment.
[Description of Notations]
1 [— An aperture plate, 5 / — A sample base, 6 / — Sample.] — The source of an oxygen radical, 2 — An RF coil, 3 — The discharge tube, 4

[Translation done.]